Synthesis of α-amino-ω-carboxypolytetrahydrofuran

Vanrenterghem, T.; Dubreuil, M.F.; Goethals, E.J.; Loontjens, T.J.

Published in:
Polymer International

DOI:
10.1002/(SICI)1097-0126(199905)48:5<343::AID-PI184>3.0.CO;2-T

Rapid Report

Synthesis of α-amino-ω-carboxy-polytetrahydrofuran

T Vanrenterghem,[1] MF Dubreuil,[1] EJ Goethals[1]* and TJ Loontjens[2]

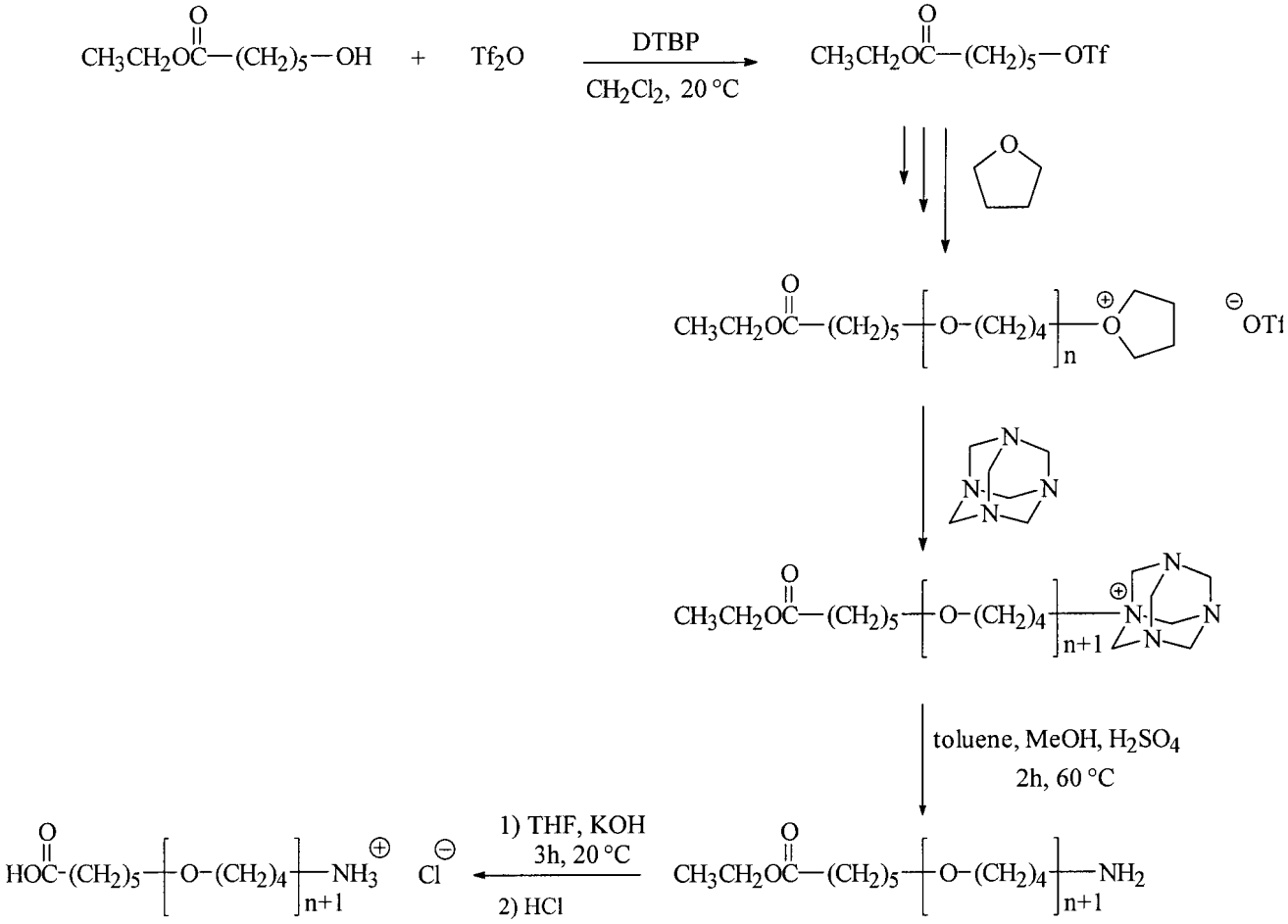
[1]*Department of Organic Chemistry, Polymer Division, University of Ghent, Krijgslaan 281, 9000 Ghent, Belgium*
[2]*DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands*

INTRODUCTION

Telechelic polymers are important building blocks for the design of new macromolecular architectures.[1] In some cases hetero-telechelic polymers, linear polymers containing two different functional end-groups on each polymer chain, may be of interest. In this paper we report a convenient method for the synthesis of α-amino-ω-carboxy-polytetrahydrofuran based on a combination of functional initiation and end-capping.

RESULTS AND DISCUSSION

In a previous paper we reported that a combination of a functionalized alcohol and trifluoromethanesulfonic acid anhydride (triflic anhydride, Tf_2O) can be used as a functional initiator system for the polymerization of tetrahydrofuran (THF).[2] This method was now applied with ethyl-6-hydroxyhexanoate (EHH) as functional alcohol leading to polyTHF carrying an ester end-group which can be hydrolyzed to the corresponding carboxylate-terminated polymer.



Scheme 1

* Correspondence to: EJ Goethals, Department of Organic Chemistry, Polymer Division, University of Ghent, Krijgslaan 281, 9000 Ghent, Belgium
(*Received 22 February 1999; accepted 24 February 1999*)

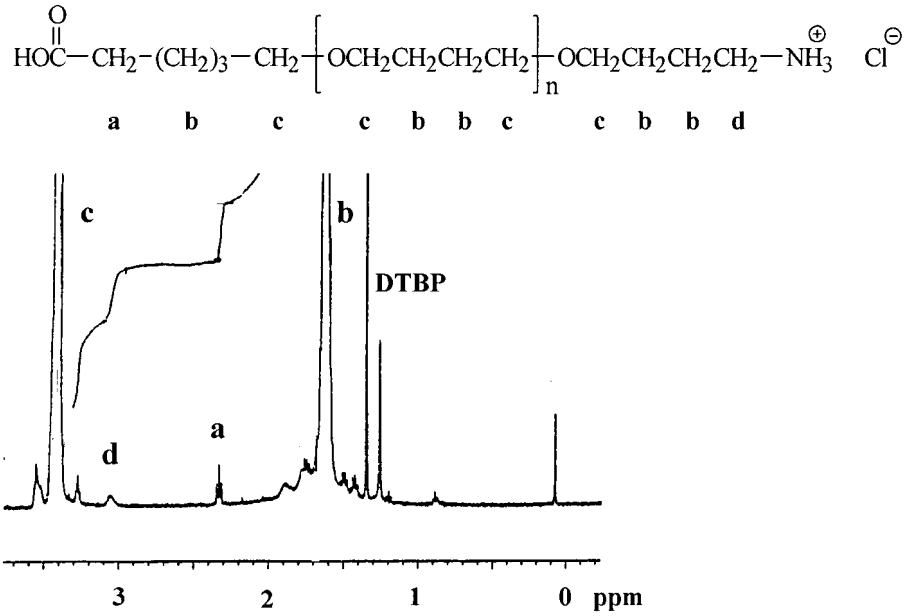


Figure 1. 360 MHz ^{1}H NMR spectrum of α-amino-ω-carboxy-polyTHF ($\overline{M}_n$ 3500 g mol^{-1}, solvent $CDCl_3$).

To introduce the amino function at the other chain end it is, in principle, possible to end-cap the living polymer with ammonia. However, it was observed that this reaction leads to a substantial fraction of coupling product resulting from reaction of the first formed primary amine with the oxonium end-group of another living polymer. A convenient method leading to the pure primary amino end-group was found to be end-capping of the living polymer with hexamethylene tetramine followed by acid hydrolysis.[3] The ester function, introduced by the initiator system, was hydrolyzed to the carboxylic function by treatment with anhydrous potassium hydroxide, as reported.[4]

The complete reaction sequence for the synthesis of the heterotelechelic polymer is given in Scheme 1. Figure 1 shows the ^{1}H NMR spectrum of a polymer with number average molecular weight 3500. The presence of multiplets of equal intensities at 2.35 and 3.1 ppm are in agreement with the presence of carboxylate and ammonium end-groups in stoechiometric amounts. As reported earlier,[2] the molecular weight of the polymers can be varied by changing the initiator concentration and/or the polymerization time. Molecular weight distributions ($\overline{M}_w/\overline{M}_n$) are typically below 1.2 (Table 1).

Table 1. Molecular weight and molecular weight distributions of α-amino-ω-carboxy-polytetrahydrofuran as a function of polymerization time. [THF] = 11.26 mol L^{-1}, [EHHOTf] = 0.0525 mol L^{-1}, solvent CH_2Cl_2. Values obtained by gel permeation chromatography

Polymerization time (min)	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
7	2000	1.19
15	3600	1.17

EXPERIMENTAL PART

Materials

Tf_2O and EHH were purified by distillation. CH_2Cl_2 was purified by general methods and used after distillation over calcium hydride. Trichloromethane was used after distillation over calcium hydride. THF was purified by general methods and used after distillation over sodium in the presence of benzophenone. 2,2-Di-*tert*-butylpyridine (DTBP) was used as received.

Synthesis

A typical synthesis of the polymer is as follows. In a dried two necked-flask of 50 mL, 7 mL of CH_2Cl_2, 500 μL of DTBP (2.23 10^{-3} mol) and 250 μL of Tf_2O (1.49 10^{-3} mol) were thermostatted at 20 °C. 239 μL of EHH (1.47 10^{-3} mol) was added dropwise under stirring. After one hour, the polymerization was started by introducing 20 mL of THF (0.247 mol). After 15 minutes, the polymerization was terminated with a solution of 0.522 g of HMTA (3.73 10^{-3} mol) in 25 mL of trichloromethane. After 10 minutes stirring at room temperature the solvents and unreacted THF were evaporated. The residue was dissolved in 10 mL of toluene, 15 mL of methanol and 1.2 g of concentrated sulfuric acid and the solution was refluxed for 2 hours. The mixture was neutralized by adding a 50% NaOH/water solution, the salts were filtered off and the filtrate was stripped to dryness on a rotary evaporator leaving 4.1 g of α-amino-ω-ester-terminated polyTHF.

4.1 g (1.18 10^{-3} mol) of the residue was added to a stirred cooled suspension (0 °C) of 2.73 g (11.75 10^{-3} mol) of potassium *tert*-butoxide in 40 mL of dry THF and 55 μL (3 10^{-3} mol) of water. The ice-bath was removed and after three hours at room temperature the mixture was acidified with concentrated hydrochloric acid. The salts were filtered off and the polymer

was precipitated in cold water, filtered off, and dried under vacuum (yield 100%).

ACKNOWLEDGEMENTS

T Vanrenterghem thanks the I.W.T. (Vlaams Instituut voor de Bevordering van het Wetenschappelijk-Technologisch onderzoek in de industrie) for a scholarship.

REFERENCES

1 Goethals EJ, *Telechelic Polymers: Synthesis and Applications*, CRC Press, Boca Raton (1989)

2 Dubreuil MF and Goethals EJ, *Macromol. Chem. Phys.* **198**:3077–3087 (1997)

3 Leir CM, Hoffmann JJ and Stark JE, EP 0 296 852 A2, 3M (1988)

4 Gassman PG and Schenk WN, *J. Org. Chem.* **42**:918–920 (1977)